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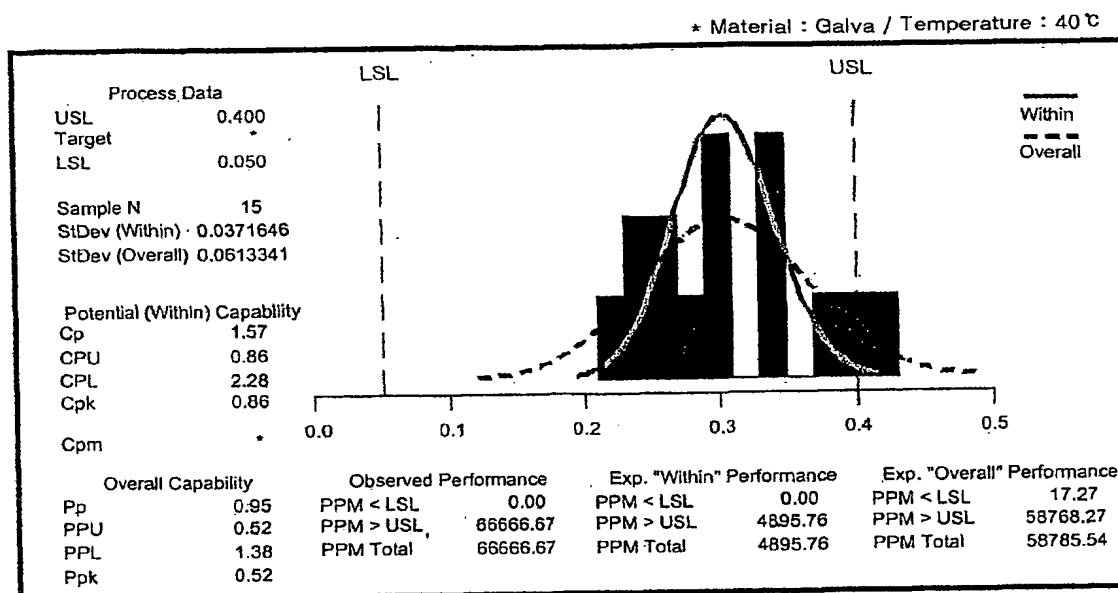
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(54) Title: COMPOSITION FOR PREPARING RIGID POLYURETHANE FOAM AND RIGID POLYURETHANE FOAM MADE THEREFROM



(57) Abstract: Composition for preparing a rigid polyurethane foam improved adhesive strength, and a rigid polyurethane foam made therefrom are provided. The composition for preparing a rigid polyurethane foam is prepared using cyclopentane system as a physical blowing agent, and polyols having a low viscosity, and has an increased adhesive strength without damages of other properties.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

COMPOSITION FOR PREPARING RIGID POLYURETHANE FOAM AND
RIGID POLYURETHANE FOAM MADE THEREFROM

TECHNICAL FIELD

5 The present invention relates to a composition for polyurethane foam, and more particularly, provides a composition for rigid polyurethane foam with improved adhesive strength, among other physical properties. The composition for the polyurethane foam has an excellent adhesive property to a material of a refrigerator.

10

BACKGROUND ART

Rigid polyurethane foam is commonly used as a material for maintaining strength of a building, a car or a refrigerator as well as an insulation material.

15 The rigid polyurethane foam is prepared by reacting suitable polyisocyanate with isocyanate group-reactive compounds in the presence of a blowing agent. As blowing agents, chlorofluorocarbon (CFC)-based compounds such as CFC-11 and hydrochlorofluorocarbon (HCFC)-based compounds such as HCFC-141b are conventionally used.

20 CFC-11 has advantage to fabricate foam having excellent insulation characteristics due to its low heat conductivity. However, as widely known, it has been prohibited to fabricate and use CFC-11, since it causes serious environmental problems such as an ozone layer destruction effect and a greenhouse effect. HCFC also contains chlorine and can also cause
25 destruction of the ozone layer, even though it is less serious compared to

CFC.

Thus, demands on a new blowing agent which may not cause the environmental problems as CFC or HCFC does are increasing. One of substitutes that have been developed is a cyclopentane-based blowing agent.

5 However, the cyclopentane-based blowing agent has a problem that it is not good in its insulation property due to high heat conductivity compared to CFC-11 or HCFC-114b. Thus, many researches are conducted to suitably select the ingredients besides a blowing agent and adjust the mixture ratio between the ingredients in the composition for preparing foam. Especially, in
10 order to increase an adhesive strength, one of critical characteristics of rigid polyurethane foam, various attempts, for example, adding several special additives thereto, have been made.

Unfortunately, however, there has been no satisfying outcome for obtaining a composition for preparing rigid polyurethane foam having an
15 improved adhesive strength without damaging other properties such as a compression strength, a dimensional stability, flowability, a demolding property or heat conductivity.

TECHNICAL GIST OF THE PRESENT INVENTION

20 Therefore, it is one object of the present invention to provide a composition for preparing rigid polyurethane foam having an increased adhesive strength while maintaining other properties.

Another object of the present invention is to provide rigid polyurethane foam fabricated from the composition for preparing rigid polyurethane foam.

25

DETAILED DESCRIPTION OF THE INVENTION

To achieve the above object, there is provided a composition for preparing rigid polyurethane foam capable of increasing an adhesive strength while maintaining its inherent physical properties by using a cyclopentane-based blowing agent and suitably adjusting the kind and content of polyol in row materials for preparing polyurethane foam. According to the present invention, the composition for preparing rigid polyurethane foam comprises:

(1) 100 weight parts of a polyol mixture consisting of:

10 40-50 weight parts of polyol B having a OH-value of 390, which is obtained by polymerization of an organic oxide using toluene diamine (TDA) of a tetra-valent functional group as an initiator; 30-40 weight parts of polyol G having a OH-value of 450, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional group; and
15 20-30 weight parts of polyol H having a OH-value of 430, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional group;

(2) 2.0-4.0 weight parts of water;

(3) 0.3-3.0 weight parts of catalyst mixture consisting of 0.1-1.0 weight
20 parts of gelling catalyst A; 0.1-1.0 weight parts of blowing catalyst B; and 0.1-1.0 weight parts of trimerizing catalyst E;

(4) 1.0-4.0 weight parts of a silicon surface-active agent;

(5) 0.5-1.5 weight parts of PFA (polyfluoroalcane);

(6) 10-20 weight parts of cyclopentane; and

25 (7) 140-170 weight parts of polyisocyanate.

If the above ingredients are used with an amount beyond the above ranges, an improved adhesive strength cannot be obtained, and other properties such as density, intensity and a demolding property will deteriorate. Thus, they are limited to the above composition range.

5 Preferably, the composition for preparing rigid polyurethane foam in accordance with the present invention comprises:

(1) 100 weight parts of a mixed polyol consisting of:

40 weight parts of polyol B having a OH-value of 390, which is obtained by polymerization of an organic oxide using toluene diamine (TDA) of a
10 tetra-valent functional group as an initiator; 30 weight parts of polyol G having a OH-value of 450, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional group; and 20-30 weight parts of polyol H having a OH-value of 430, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional
15 group;

(2) 2.0 weight parts of water;

(3) 1.5 weight parts of catalyst mixture consisting of 0.6 weight parts of gelling catalyst A; 0.4 weight parts of blowing catalyst B; and 0.5 weight parts of trimerizing catalyst E;

20 (4) 2.0 weight parts of a silicon surface-active agent;

(5) 1.0 weight parts of PFA (polyfluoroalcane);

(6) 17 weight parts of cyclopentane; and

(7) 148.2 weight parts of polyisocyanate.

Among the above composition, combination of polyols makes the most
25 direct influence on the increase of the adhesive strength. Combination of

polyols used in the present invention will be described as follows.

Polyol

Currently, polyol commonly used in the polyurethane industry is a
5 poly-functional alcohol with an ether (R-O-R') structure, which is obtained by
polymerization of an organic oxide using a compound having two or more
active hydrogens as an initiator.

Eight types of polyol A - I were used in experimentation of the present
invention, as follows.

10 Polyol A used in the present invention is obtained by polymerization of
an organic oxide using sorbitol of a hexa-valent functional group as an initiator.

Polyol B, which is used in the present invention, is obtained by
polymerization of an organic oxide using TDA (toluenediamine) of a
tetra-valent functional group as an initiator, and has an OH-value of 390.

15 Polyol C is obtained by using the same method as that of polyol B
except for using TDA having higher viscosity and OH value than that used for
polyol B.

Polyol D is obtained by polymerization of an organic oxide using ester of
bi-valent functional group as an initiator.

20 Polyol E is obtained by polymerization of an organic oxide using
glycerine of a tri-valent functional group as an initiator.

Polyol F is obtained by polymerization of an organic oxide using MDA
(methyl diisocyanate) of a tetra-valent functional group as an initiator.

Polyol G, which is used in the present invention, is obtained by mixing
25 sucrose of an octa-valent functional group and glycerine of a tri-valent

functional group, and has an OH-value of 450.

Polyol H, which is used in the present invention, is obtained by mixing sucrose of an octa-valent functional group and glycerin of a tri-valent functional group, and has 430 OH-value, slightly lower viscosity and OH-value than those
5 of polyol G.

Polyol I is obtained by polymerization of an organic oxide using a TEOA (Triethanol amine) of a tri-valent functional group as an initiator.

Silicon surface-active agent

10 In the present invention, the silicon surface-active agent improves a mixing efficiency in mixture having very low mutual solubility and stabilizes a cell by inhibiting irregular formation and growth of air foam, as in a general rigid polyurethane foam. The silicon surface-active agent used in the present invention includes B-8462, L-6900, and the like, which may be used in the
15 amount of 2-4 parts by weight, and preferably, 2.0 parts by weight, based on 100 weight parts of polyol.

Polyfluoroalkane/perfluoro carbon

In order to overcome the high heat conductivity, the worst shortcomings
20 of the cyclopentane group, researches have been made on an MCR (Micro-Cellular Rigid) foam technique. Accordingly, several types of alkylene oxide systems have been developed to obtain generalization of a corresponding composition. Polyfluoroalkane increase a nucleating effect at an initial stage of reaction to harden an initially generated micro cell, whereby the
25 initial cell size is maintained to be fine and an insulation effect is improved. In

the present invention, polyfluoroalkane is used in the amount of 0.5-1.5 parts by weight, and preferably, 1.0 parts by weight, based on 100 weight parts of polyol mixture.

5 Catalyst

A catalyst shortens a reaction time in formation of foams, and controls a flowability of foams in blowing of foams, namely, rising of foams. The catalyst used in the present invention is roughly divided into three kinds, that is, a blowing catalyst, a gelling catalyst and a trimerizing catalyst. The catalyst
10 needs to be suitably controlled in its amount used according to a shape and a structure of an actual refrigerator. In the experiments herein, 5 types of catalysts were combined to be used, of which catalysts B, G and H are used in the present invention. This will now be described in detail.

The catalyst A used in the composition according to the present
15 invention is a gelling catalyst that affects foam and reactivity, such as DMCHA (N,N-dimethylcyclohexylamine). The catalyst A attacks methyl diisocyanate (MDI) to make it react with polyol and thereby to produce polyurethane resin. Following examples are taken:

DMCHA: PC-8, PC-33, TC-DMCH, KAO-10

20 TMHDA: PC-6, TC-MR, KAO-1

TEDA: DABCO33LV, NIAXA-33, TC TEA-L33

The catalyst B used in the composition according to the present invention is a blowing catalyst, such as pentamethyl diethylene triamine (PMDETA). This catalyst facilitates a reaction between water and methyl
25 diisocyanate (MDI) and supplies heat required for foaming, to accelerate a

resin reaction between polyol and MDI. Following examples are taken:

PMDETA: PC-5, TC-DT, KAO-3

BDMEE: DABCO BL-11, TC-ET, NIA X A-1

The catalyst C is a mixed catalyst obtained by mixing DMCHA and
5 PMDETA in the ratio of 3:1.

The catalyst D is an acid block type blowing catalyst which generates much CO₂ gas by affecting an initial reactivity.

The catalyst E used in the composition according to the present invention is a trimerizing catalyst for a reaction and trimerization of MDI.

10 Following examples are taken:

TMR-2, TMR-13, TMR-30

PC-41, KAO-14, TC-TRC

Isocyanate

15 Any isocyanate which can be generally used in preparing polyurethane foam may also be available in the present invention. It may be preferable that the index of isocyanate is not high, such as 1.0-1.2 of the general polyurethane foam. For example, methyl diisocyanate (MDI) can be used. Isocyanate may be used in the amount of 140-170 parts by weight, based on 100 weight parts of a
20 polyol mixture

Chemical blowing agent

In the present invention, water was used as a chemical blowing agent in the amount of 2.0-4.0 parts by weight, and preferably, 2.0 parts by weight,
25 based on 100 weight parts of a polyol mixture.

Physical blowing agent.

Cyclopentane was used as a physical blowing agent for a composition of the present invention. Besides, HCFC-114b and CFC-11 were used for
 5 comparison in the experiments.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a testing method to measure an adhesive strength;

Figure 2 is a graph showing a process capability analysis of foam in
 10 accordance with Example 2 of the present invention; and

Figure 3 is a graph showing a process capability analysis of foam in accordance with Example 3 of the present invention; and

BEST MODE FOR CARRYING OUT THE PREFERRED15 EMBODIMENTS

Preferred embodiments will now be described but the present invention is not limited thereto.

[Table 1]

		Examples				
		Cyclopentane group			HCF-141b group	CFC-11 group
		1	2	3	4	5
Row material	Polyol A	40			40	30
	Polyol B	30	40	40	30	20
	Polyol C		30			
	Polyol D	10			10	
	Polyol E	20			20	10
	Polyol F					20
	Polyol G		30	30		10
	Polyol H			30		
	Polyol I					10
	Water	2.0	2.0	2.0	2.0	2.0

	Catalyst A		0.6	0.6	0.5	
	Catalyst B		0.4	0.4	0.6	
	Catalyst C	0.6				1.0
	Catalyst D	0.4				0.5
	Catalyst E	0.5	0.5	0.5	0.4	0.5
	Silicon surface-active agent	2.0	2.0	2.0	2.0	2.0
	PFA		1.0	1.0		
	Physical blowing agent	17	17	17	40	30
	Polyisocyanate	148.2	148.2	148.2	140	140

In Table 1, the unit of injection amount is pbw (parts by weight).

Foam was prepared by sufficiently mixing the components in the compositions according to Examples 1-5 of Table 1 in such a proper way as to completely exhibit physical properties of each component, according to a general polyurethane foam preparing method.

A core density, a dosage (Just Pack), K-factor, a demolding property and an adhesive strength of the obtained foams of five types were measured, and the result was shown in Table 2. The adhesive strength was measured, as followings.

Measurement of adhesive strength

A test sample of a material having the size of 100mm x 40mm with a hole of Φ 4.5 (Galva, the weakest among refrigerator materials) was used for testing adhesive strength. The density of polyurethane foam was 32-34 kg/m² in case of the cyclopentane-based foam of Examples 1-3, 30-32 kg/m² in case of the HCFC-141b-based foam of Example 4, and 29-31 kg/m² in case of the CFC-11-based foam of Example 5. The number of test samples was 15.

As shown in Figure 1, a material was attached to a Brett mold and foamed at the core density of polyurethane foam. The material-attached positions were 150mm, 500mm and 850mm of the total length of 1100mm, on

the basis of a lower end. 5 minutes later, it was demolded and left for one hour at a room temperature. A force applied to detach the material by using a push-pull gage was measured to evaluate an adhesive strength and the result was shown in Table 2. Figures 2 and 3 are graphs showing a process capability analysis of foams according to Examples 2 and 3, indicating a distribution of low and high adhesive strengths.

[Table 2]

	Example 1	Example 2	Example 3	Example 4	Example 5
Core density (kg/m ³)	31.54	29.94	30.51	28.90	27.50
Injection amount (g)	517	495	497	475	425
Compression strength (kg/cm, 25°C)	1.45	1.44	1.52	1.51	1.15
K-factor (kcal/m·hr·°C)	0.01654	0.01644	0.01668	0.01545	0.01567
Demolding property (%)	2.19	2.10	1.87	1.95	2.11
Adhesive strength (kg/cm ²)	0.112	0.085	0.304	0.091	0.094

As noted from Table 2, the prepared polyurethane foams differ in the properties and the characteristics depending on their compositions. As a blowing agent, Examples 1 to 3 use cyclopentane groups, Example 4 uses HCFC-141b, and Example 5 uses CFC-11. Since the construction of the systems differs depending on the type of the blowing agent used, there are differences in the insulation characteristics and dosage (Jus Pack).

A characteristic that the present invention aims to improve is the adhesive strength. As noted from the property of Example 3, the adhesive strength is as high as to be almost double compared to other Examples. Besides the adhesive strength, other properties of the polyurethane foam prepared from the composition of the Example 3 are the same as those of the Examples 1 and 2, and also do not make a big difference with the properties of

Examples 4 and 5.

Especially, in view that Example 2 and 3 have a difference only in the composition of the basic polyol, it can be concluded that the composition of polyol has a large effect on the adhesive strength. The higher adhesive strength in Example 3 than that of other systems is due to using a polyol component obtained by using a TDA with low viscosity as an initiator. However, this component is disadvantageous in that it has a low demolding property, in spite of the excellent heat conductivity and adhesive strength. Thus, a sucrose/glycerin with lower viscosity than that used in Example 2 was used to improve a flowability and stability of prepared polyurethane foam. In addition, this component exhibits excellent adhesive strength and demolding property. Meanwhile, when using sucrose/glycerin with high viscosity, the adhesive strength and flowability were relatively low, but heat conductivity and demolding property were good.

From the results in Table 2, it can be known that the composition for preparing polyurethane foam in accordance with Example 3 shows increased adhesive strength without degradation of other properties such as the demolding property, the heat conductivity and the like.

INDUSTRIAL APPLICABILITY

As so far described, the composition for preparing rigid polyurethane foam has the following advantages. That is, for example, since the composition uses water and cyclopentane as a blowing agent, there is no possibility of damaging an environment as the composition using conventional CFC-based or HCFC-based blowing agent does. In addition, since the adhesive strength is

improved nearly double the existing composition, with maintaining the major characteristics of the foam, the composition can be suitably applied to construct an insulation material, and especially, a refrigerator.

CLAIMS

1. A composition for preparing rigid polyurethane foam comprises:

(1) 100 weight parts of a polyol mixture consisting of:

5 40-50 weight parts of polyol B having a OH-value of 390, which is obtained by polymerization of an organic oxide using toluene diamine (TDA) of a tetra-valent functional group as an initiator; 30-40 weight parts of polyol G having a OH-value of 450, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional group; and
10 20-30 weight parts of polyol H having a OH-value of 430, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional group;

(2) 2.0-4.0 weight parts of water;

(3) 0.3-3.0 weight parts of catalyst mixture consisting of 0.1-1.0 weight
15 parts of gelling catalyst A; 0.1-1.0 weight parts of blowing catalyst B; and 0.1-1.0 weight parts of trimerizing catalyst E;

(4) 1.0-4.0 weight parts of a silicon surface-active agent;

(5) 0.5-1.5 weight parts of PFA (polyfluoroalthane);

(6) 10-20 weight parts of cyclopentane; and

20 (7) 140-170 weight parts of polyisocyanate.

2. A composition for preparing rigid polyurethane foam according to claim 1, comprises;

(1) 100 weight parts of a mixed polyol consisting of:

25 40 weight parts of polyol B having a OH-value of 390, which is obtained

by polymerization of an organic oxide using toluene diamine (TDA) of a tetra-valent functional group as an initiator; 30 weight parts of polyol G having a OH-value of 450, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional group; and 20-30 weight parts of polyol H having a OH-value of 430, which is obtained by mixing sucrose of a octa-valent functional group and glycerin of tri-valent functional group;

(2) 2.0 weight parts of water;

(3) 1.5 weight parts of catalyst mixture consisting of 0.6 weight parts of gelling catalyst A; 0.4 weight parts of blowing catalyst B; and 0.5 weight parts of trimerizing catalyst E;

(4) 2.0 weight parts of a silicon surface-active agent;

(5) 1.0 weight parts of PFA (polyfluoroalthane);

(6) 17 weight parts of cyclopentane; and

(7) 148.2 weight parts of polyisocyanate.

3. A rigid polyurethane foam prepared by the composition of claim 1 or 2.

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FIG. 1

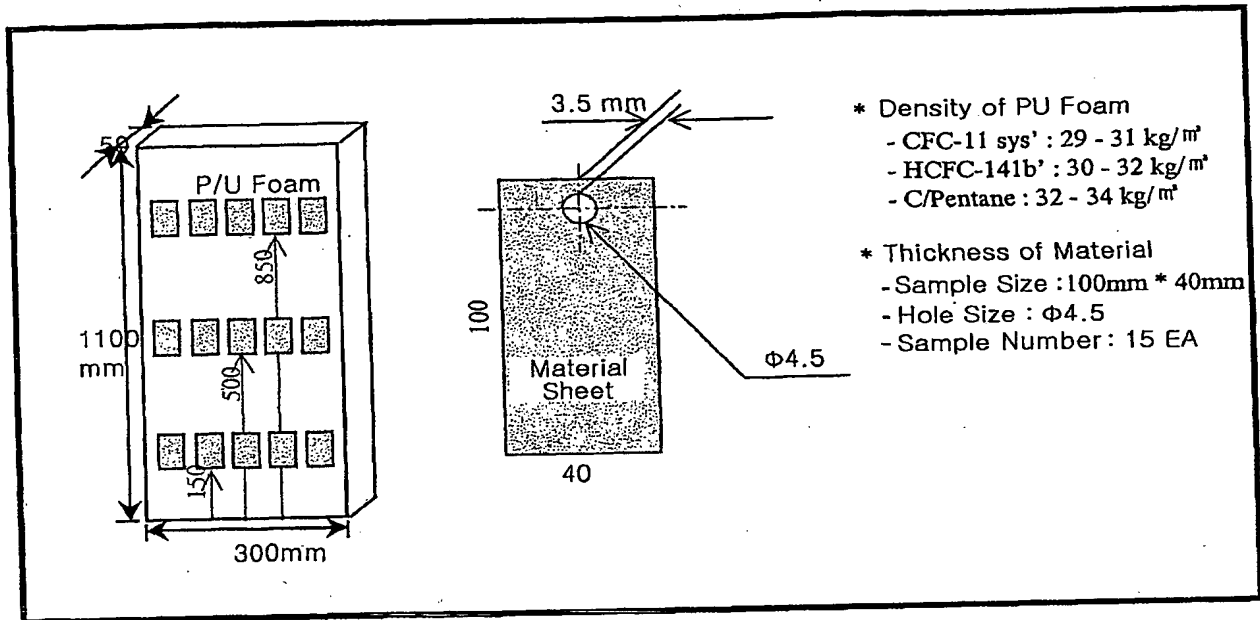
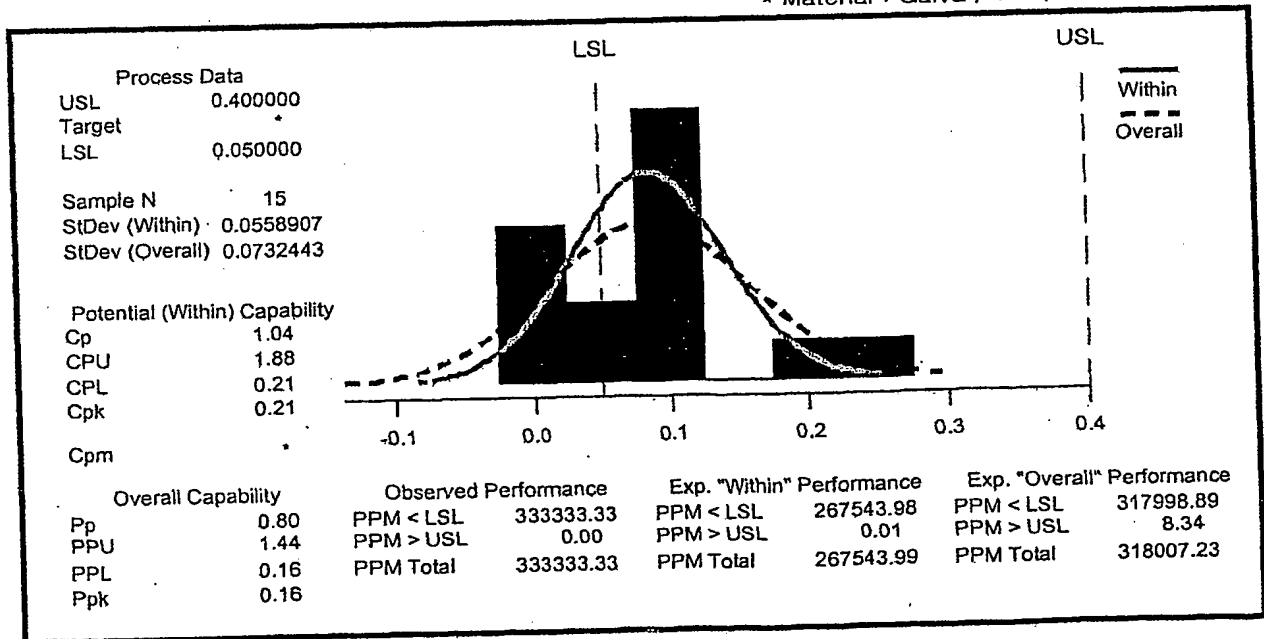


FIG. 2

* Material : Galva / Temperature : 40 °C

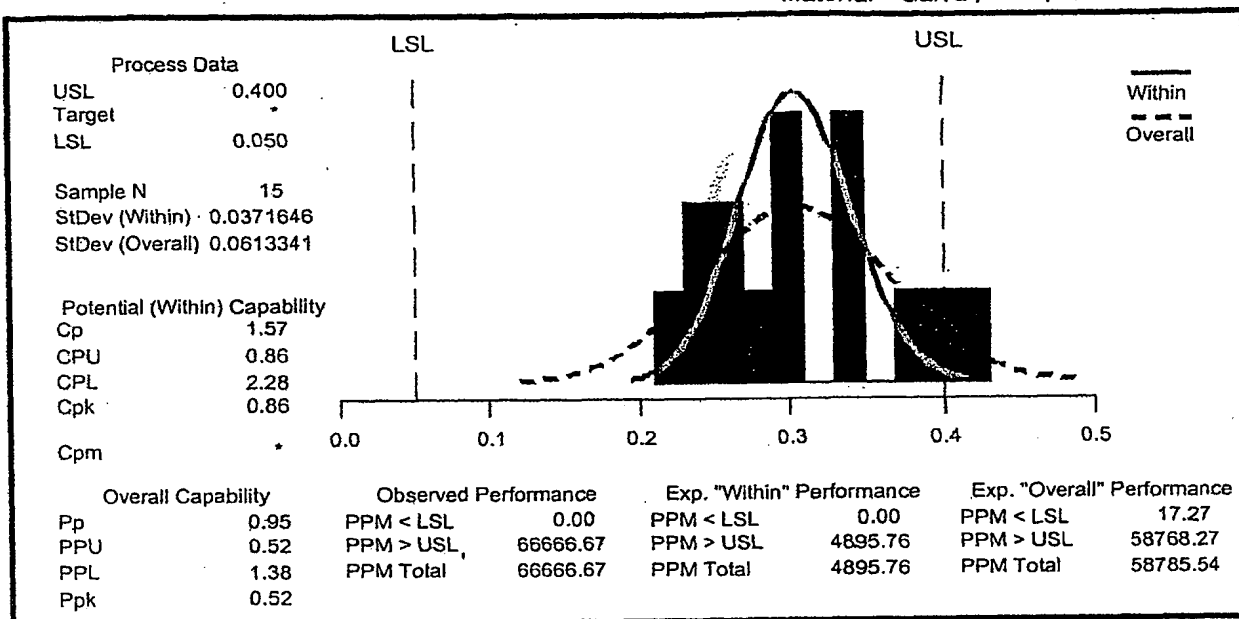


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FIG. 3

* Material : Galva / Temperature : 40 °C



INTERNATIONAL SEARCH REPORT

Additional application No.
PCT/KR03/00109

A. CLASSIFICATION OF SUBJECT MATTER IPC7 C08G 18/00, 18/18, 18/50 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08G Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean patents and applications for inventions since 1975 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) STN(CA) "polyol and toluene diamine and sucrose" and NPS "polyol and toluene diamine and sucrose"		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5840781 A (Dietrich et al.) 24 NOV 1998 See column 1 line 44-62, claim 1-8, abstract, example 1	1-3
A	US 5883146 A (Tucker) 16 MAR 1999 See column 16 line 21-43	1-3
A	US 5886062 A (Dietrich et al.) 23 MAR 1999 See column 2 line 42 - column 4 line 33, claim 1, 5, 7, abstract	1-3
A	US 6107359 A (Dietrich et al.) 22 AUG 2000 See claim 1, 6, example 1	1-3
A	US 4780482 A (Krueger) 25 OCT 1988 See the whole document	1-3
A	US 4521548 A (Christen et al.) 4 JUN 1985 See claim 1, 7, 9, 10, example 1, 3	1-3
A	EP 1018526 A (El Ghobary et al.) 12 JUN 2000 See claim 4	1-3
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 15 OCTOBER 2003 (15.10.2003)		Date of mailing of the international search report 16 OCTOBER 2003 (16.10.2003)
Name and mailing address of the ISA/KR  Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140		Authorized officer LEE, Dong Wook Telephone No. 82-42-481-8115 

INTERNATIONAL SEARCH REPORT

nal application No.

PCT/KR03/00109

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1178062 A (Murayama et al.) 6 FEB 2002 See the whole document	1-3
A	EP 1172388 A (Nodelman et al.) 16 JAN 2002 See the whole document	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR03/00109

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5840781 A	24-11-1998	EP 805831 A1 BR 9606846 A	12-11-1997 25-11-1997
US 5883146 A	16-03-1999	CA 2165116 AA	30-06-1996
US 5886062 A	23-03-1999	DE 19634700 A1 CA 2213925 AA JP 10101763 A2 EP 826708 A1	05-03-1998 28-02-1998 21-04-1998 04-03-1998
US 6107359 A	22-08-2000	NONE	
US 4780482 A	25-10-1988	CA 1307372 A1 EP 293589 A1	08-09-1992 07-12-1988
US 4521548 A	04-06-1985	NONE	
EP 1018526 A1	12-07-2000	JP 2000204135 A2 KR 2000053377 A CN 1267674 A MX 200000238 A	25-07-2000 25-08-2000 27-09-2000 08-03-2003
EP 1178062 A1	06-02-2002	US 2002035166 A1 JP 2002114840 A2 CN 1339516 A	21-03-2002 16-04-2002 13-03-2002
EP 1172388 A1	16-01-2002	US 6586487 B1 BR 2001002768 A JP 2002053641 A2 CN 1333302 A	01-07-2003 26-01-2002 19-02-2002 30-01-2002
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